REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
06-04-2008	Final Report	1-Jun-2004 - 31-Dec-2007

4. TITLE AND SUBTITLE

Shock Tube Measurements of Ignition Processes and Spray-Shock Wave Interactions

5a. CONTRACT NUMBER
W911NF-04-1-0138

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

6. AUTHORS

R. K. Hanson, D. F. Davidson

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES

Stanford University
Office of Sponsored Research
Board of Trustees of the Leland Stanford Junior University
Stanford, CA 94305 -

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
45728-EG.13

12. DISTRIBUTION AVAILIBILITY STATEMENT

Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

We report results of high-temperature shock tube research aimed at improving knowledge of the combustion behavior of diesel, jet and related fuels. Research was conducted in four Stanford shock tube facilities and focused on the following topics: (1) development of the aerosol shock tube; (2) ignition delay time measurements of gaseous jet fuels (JP-8 and Jet-A) and surrogate components at high pressures and low temperatures; (3) laser absorption measurements of species time-histories for OH radicals and alkanes; (4) ignition delay times of n-dodecane, jet fuel and diesel using the aerosol shock tube technique; and (5) improving shock tube performance and modeling.

15. SUBJECT TERMS

Shock Tube, jet fuel chemistry, ignition delay time, laser absorption techniques, surrogate fuels

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Ronald Hanson
U	U	U	SAR		19b. TELEPHONE NUMBER 650-723-6850

Report Title

Shock Tube Measurements of Ignition Processes and Spray-Shock Wave Interactions

ABSTRACT

We report results of high-temperature shock tube research aimed at improving knowledge of the combustion behavior of diesel, jet and related fuels. Research was conducted in four Stanford shock tube facilities and focused on the following topics: (1) development of the aerosol shock tube; (2) ignition delay time measurements of gaseous jet fuels (JP-8 and Jet-A) and surrogate components at high pressures and low temperatures; (3) laser absorption measurements of species time-histories for OH radicals and alkanes; (4) ignition delay times of n-dodecane, jet fuel and diesel using the aerosol shock tube technique; and (5) improving shock tube performance and modeling.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

H. Li, Z. C. Owens, D. F. Davidson, R. K. Hanson, "A Simple Reactive Gasdynamic Model for the Computation of Gas Temperature and Species Concentration behind Reflected Shock Waves," International Journal of Chemical Kinetics 40 (2008) 189-198.

S. S. Vasu, D. F. Davidson, R. K. Hanson, "Jet Fuel Ignition Delay Times: Shock Tube Experiments over Wide Conditions and Surrogate Model Predictions," Combustion and Flame 152 (2008) 125-143.

D. F. Davidson, D. R. Haylett, R. K. Hanson, "Development of an Aerosol Shock Tube for Kinetic Studies of Low-Vapor-Pressure Fuels", Combustion and Flame, in press.

D. F. Davidson, M. A. Oehlschlaeger, R. K. Hanson, "Methyl Concentration Time Histories during iso-Octane and n-Heptane Oxidation," Proceedings of the Combustion Institute 31 (2007) 321-328.

T. C. Hanson, D. F. Davidson, R. K. Hanson, "Shock Induced Behavior in Micron-Sized Water Aerosols," Physics of Fluids 19 (2007) 056104.

H. Li, A. Farooq, J. B. Jeffries, R. K. Hanson, "Near-infrared Diode Laser Absorption Sensor for Rapid Measurements of Temperature and Water Vapor in a Shock Tube," Applied Physics B 89 (2007) 407-416.

A. E. Klingbeil, J. B. Jeffries, R. K. Hanson, "Temperature-Dependent Mid-IR Absorption Spectra of Gaseous Hydrocarbons," J. Quantitative Spectroscopy and Radiative Transfer 107 (2007) 407-420.

E. L. Petersen, R. K. Hanson, "Measurement of Reflected-Shock Bifurcation over a Wide Range of Gas Composition and Pressure," Shock Waves 15 (2006) 333-340.

D. F. Davidson, B. M. Gauthier, R. K. Hanson, "Shock Tube Ignition Measurements of Iso-Octane/Air and Toluene/Air at High pressures," Proceedings of the Combustion Institute 30 (2005) 1175-1182.

V. Vasudevan, D. F. Davidson, R. K. Hanson, "Shock Tube Measurements of Toluene Ignition Times and OH Concentration Time Histories," Proceedings of the Combustion Institute 30 (2005) 1155-1163.

Number of Papers published in peer-reviewed journals: 11.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

J. B. Jeffries, A. Klingbeil, E. Barbour, A. Farooq, R. K. Hanson, “Mid-Infrared Gas Sensing for Combustion Applications” submitted to Laser Applications to Chemical, Security and Environmental Applications (LACSEA), OSA, St Petersburg FL, March 2008.
G. A. Pang, D. F. Davidson, R. K. Hanson, “Experimental Study and Modeling of Shock Tube Ignition Delay Times for Hydrogen-Oxygen-Argon Mixtures at Low Temperatures,” Paper 08S-10, Western States Section/Combustion Institute Spring Meeting, Los Angeles, March 2008.
D. F. Davidson, R. K. Hanson, “Recent Advances in Shock Tube/Laser Diagnostics Methods for Improved Chemical Kinetics Measurements,” Paper 08S-01, Western States Section/Combustion Institute Spring Meeting, Los Angeles, March 2008.
S. S. Vasu, D. F. Davidson, R. K. Hanson, “OH Time-History Absorption Measurements at High Pressure and Temperatures Behind Reflected Shocks During Methylcyclohexane Oxidation,” Paper 08S-13, Western States Section/Combustion Institute Spring Meeting, Los Angeles, March 2008.
G.A. Pang, D.F. Davidson and R.K. Hanson, “Shock Tube Ignition Delay Times for Hydrogen-Oxygen-Argon Mixtures at Low Temperatures and Elevated Pressures,” Paper No. 07F-12, Western States Section/Combustion Institute Fall Meeting, Livermore CA, October 2007.
S. S. Vasu, D. F. Davidson, R. K. Hanson, “Jet Fuel Ignition Delay Times and Modeling: Studies at High Pressures and Low Temperatures in a Shock Tube,” Paper No. AIAA-2007-5671, 43rd AIAA Joint Propulsion Conference, July 2007.
S. S. Vasu, D. F. Davidson, R. K. Hanson, “High Pressure Shock Tube Experiments and Modeling of n-Dodecane/Air Ignition,” Paper No. P-2730, 26th International Symposium on Shock Waves, July 2007.
A. Farooq, J. Li, J. B. Jeffries, R. K. Hanson, “Measurements of CO2 and H2O near 2.7 microns using Tunable Diode Laser Absorption,” AIAA 2007-5015 43rd AIAA Joint Propulsion Conference, Cincinnati, July 2007.
H. Li, A. Farooq, R. D. Cook, D. F. Davidson, J. B. Jeffries, R. K. Hanson, “A Diode Laser Absorption Sensor for Rapid Measurements of Temperature and Water Vapor in a Shock Tube,” Paper No. P-2660, 26th International Symposium on Shock Waves, July 2007.
D. R. Haylett, D. F. Davidson, R. K. Hanson, “Development of an Aerosol Shock Tube for Kinetic Studies of Low-Vapor-Pressure Fuels,” Paper No. AIAA-2007-5678, 43rd AIAA Joint Propulsion Conference, July 2007.
S. S. Vasu, D. F. Davidson, R. K. Hanson, “Jet Fuel Ignition Delay Times: Shock Tube Investigations at High Pressures,” Paper No. 129, 21st ICDERS Meeting, Poitiers France, July 2007.
S. S. Vasu, N. N. Parikh, D. F. Davidson, R. K. Hanson, “Methylcyclohexane Oxidation: Shock Tube Experiments and Modeling over a Wide Range of Pressures and Temperatures,” Paper No. D17, 5th U. S. Combustion Meeting, San Diego, March 2007.
A. E. Klingbeil, J. M. Porter, J. B. Jeffries, R. K. Hanson, "Two-Wavelength Mid-IR Absorption Sensor for Simultaneous Temperature and n-Heptane Concentration Experiments” Paper No. GO3 at 5th U. S. Combustion Meeting, San Diego, March 2007.
S. S. Vasu, D. F. Davidson, R. K. Hanson, “Shock Tube Ignition Delay Times and Modeling of Jet Fuel Mixtures,” Paper AIAA-2006-4402, 42nd AIAA/ASME/SAE/ASEE Joint Propulsion Conference, Sacramento CA, July 2006.
D. F. Davidson, M. A. Oehlschlaeger, R. K. Hanson, “Methyl Concentration Time Histories during iso-Octane and n-Heptane Oxidation,” Paper 05S-61, Western States Section/Combustion Institute Fall Meeting, Stanford CA, October 2005.
S. S. Vasu, D. F. Davidson, R. K. Hanson, “Shock Tube Measurements and Modeling of Ignition Delay Time in Lean Iso-Octane/Air,” Int. Symp. Shock Waves 25, June 2005.
T. C. Hanson, D. F. Davidson, R. K. Hanson, “Shock Tube Measurements of Water and n-Dodecane Droplet Evaporation Behind Shock Waves”, Paper 2005-0350, 43rd Aerospace Meeting and Exhibit, January 2005, Reno NV.

On-Line Reports
D. F. Davidson and R. K. Hanson, “Fundamental Kinetics Database Utilizing Shock Tube Measurements, Vol. 2: Concentration Time-History Measurements” Mech. Eng. Dept. Report, Stanford University, December 2006.
D. F. Davidson and R. K. Hanson, “Fundamental Kinetics Database Utilizing Shock Tube Measurements, Vol. 1: Ignition Delay Time Measurements” Mech. Eng. Dept. Report, Stanford University, November 2005, available at http://hanson.stanford.edu/.

Number of Papers published in non peer-reviewed journals: 19.00

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

S. S. Vasu, D. F. Davidson, Z. Hong, V. Vasudevan, R. K. Hanson, "n-Dodecane Oxidation at High Pressures: Measurements of Ignition Delay Times and OH Concentration Time-Histories," accepted for publication, 32nd Combustion Symposium, April 2008.
G. A. Pang, D. F. Davidson, R. K. Hanson, "Experimental Study and Modeling of Shock Tube Ignition Delay Times for Hydrogen-Oxygen-Argon Mixtures at Low Temperatures," accepted for publication, 32nd Combustion Symposium, April 2008.
A. Farooq, D. F. Davidson, R. K. Hanson, L. K. Huynh, A. Violi, "An Experimental and Computational Study of Methyl Ester Decomposition Pathways using Shock Tubes," accepted for publication, 32nd Combustion Symposium, April 2008.
A. E. Klingbeil, J. Porter, J. B. Jeffries, R. K. Hanson "Two-wavelength mid-IR absorption diagnostic for simultaneous measurement of temperature and hydrocarbon fuel concentration," accepted for publication, 32nd Combustion Symposium, April 2008.
D. R. Haylett, D. F. Davidson, R. K. Hanson, "Application of an Aerosol Shock Tube to the Measurement of Diesel Ignition Delay Times," accepted for publication, 32nd Combustion Symposium, April 2008.
A. E. Klingbeil, D. F. Davidson, J. B. Jeffries, R. K. Hanson, "Two-Wavelength Mid-IR Diagnostic for Temperature and n-Dodecane Concentration in an Aerosol Shock Tube," accepted for publication, Applied Physics B.

Number of Manuscripts: 5.00

Number of Inventions:

Graduate Students

NAME	PERCENT_SUPPORTED
Subith Vasu	0.50
Daniel Haylett	0.50
FTE Equivalent:	**1.00**
Total Number:	**2**

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Ronald Hanson	0.05	Yes
FTE Equivalent:	**0.05**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
Andrew Zimbroff	0.00
FTE Equivalent:	**0.00**
Total Number:	**1**

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	1.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	1.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	1.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME
Subith Vasu
Daniel Haylett
Total Number: **2**

Names of personnel receiving PHDs

NAME
Tom Hanson
Total Number: **1**

Names of other research staff

NAME	PERCENT_SUPPORTED	
David Davidson	0.10	No
FTE Equivalent:	**0.10**	
Total Number:	**1**	

Sub Contractors (DD882)

Inventions (DD882)

HTGL

Final Progress Report

ARO Grant
W911NF-04-1-0138

Shock Tube Measurements of Ignition Processes and Spray-Shock Wave Interactions

Prepared for:

DEPARTMENT OF THE ARMY
Dr. Ralph Anthenien Jr., Program Manager

For the period August 1, 2004-December 31, 2007

Submitted by:
Professor R. K. Hanson, PI
Mechanical Engineering Department
Stanford University, Stanford, CA 94305
rkhanson@stanford.edu
650-723-6850

March 2008

HIGH TEMPERATURE GASDYNAMICS LABORATORY
Mechanical Engineering Department
Stanford University, Stanford CA 94305

Contents

SHOCK TUBE MEASUREMENTS OF IGNITION PROCESSES AND SPRAY-SHOCK WAVE INTERACTIONS

Ronald Hanson
Department of Mechanical Engineering
Stanford University, Stanford, CA 94305

SUMMARY

This report summarizes research performed at Stanford University from 2004 to 2007 in the areas of shock tube measurements of ignition processes and spray-shock wave interactions. Results of high-temperature shock tube research aimed at improving knowledge of the combustion behavior of diesel, jet and related fuels are described. Research was conducted in four Stanford shock tube facilities and focused on the following topics: ignition delay time measurements of gaseous jet fuels (JP-8 and Jet-A) as well as surrogate fuel components at high pressures and low temperatures; the development of an aerosol shock tube technique to access low-vapor-pressure fuels; laser absorption measurements of fuel and radical species time-histories during oxidation and pyrolysis; and the development of new methods to extend and improve shock tube operation and modeling.

STATEMENT OF THE PROBLEM STUDIED

Validation of the predictive power of large reaction mechanisms and development of reduced mechanisms describing the pyrolysis, oxidation and ignition of practical fuels require a reliable database of experimental combustion targets such as ignition delay times and species concentration time-histories. Only a limited amount of shock tube ignition time data presently exist for the heavier practical fuels and fuel components, and virtually no shock tube species time-history measurements exist for reactants (practical fuels and pure surrogate components), small transient radical species (such as OH, HCO, CH_3, and benzyl) and combustion products (H_2O, CO and CO_2). To help remedy this deficiency, we have developed a unique database of ignition time and species concentration time-history measurements derived from in-house shock tube studies. This database covers fuel components, such as n-alkanes, branched alkanes, cyclo-alkanes, alkenes and aromatics, as well as surrogate mixtures, and practical fuels including gasoline, jet fuel and diesel. We have used this database to validate and refine existing reaction mechanisms and to develop and test proposed surrogate fuel mixtures; and of course we will make this database available to others.

To investigate this problem we have used a three-pronged approach. The first is the continued development and use of an aerosol shock tube to study ignition processes in low-vapor-pressure fuels. The second is the use of modified shock tube driver geometries and tailored gas mixtures to extend test times and enable study of ignition processes at low temperatures. The third is the use of visible/ultraviolet laser absorption methods and the development of mid-IR laser absorption schemes to measure species concentration time-histories of fuel components, intermediate species and products and for the determination of critical reaction rates.

SUMMARY OF THE MOST IMPORTANT RESULTS

Ignition Delay Time and OH Time-History Measurements in MCH and n-Heptane

We have measured OH concentration time-histories in methylcyclohexane (MCH) and n-heptane oxidation behind reflected shocks waves using a heated, high pressure shock tube. Measurements were made over temperatures of 1121 to 1332 K, at pressures near 15 atm, for an equivalence ratio of 0.5 in Argon bath gas. Initial fuel concentrations of 1000 ppm, and 750 ppm were used in these experiments. Measurements were conducted using narrow-linewidth ring-dye laser absorption near the R branchhead of the OH A-X (0, 0) system at 306.47 nm. See Figs. 1 and 2. Current measurements together with our recent results for n-dodecane further improve current understanding of high-pressure, high-temperature oxidation chemistry, and provide excellent validation targets for kinetic mechanisms. Detailed comparisons have been made with the predictions of various kinetic mechanisms, and sensitivity analysis has been used to analyze the high temperature oxidation pathways for these three important reference fuel components. Suggestions to improve model performance have been made by examining key reactions that influence OH concentrations. Our current results provide the first quantitative measurements of OH time histories during high pressure oxidation of these fuels, and hence are a critical step toward accurate kinetic models. Further description can be found in S. S. Vasu et al. (2008).

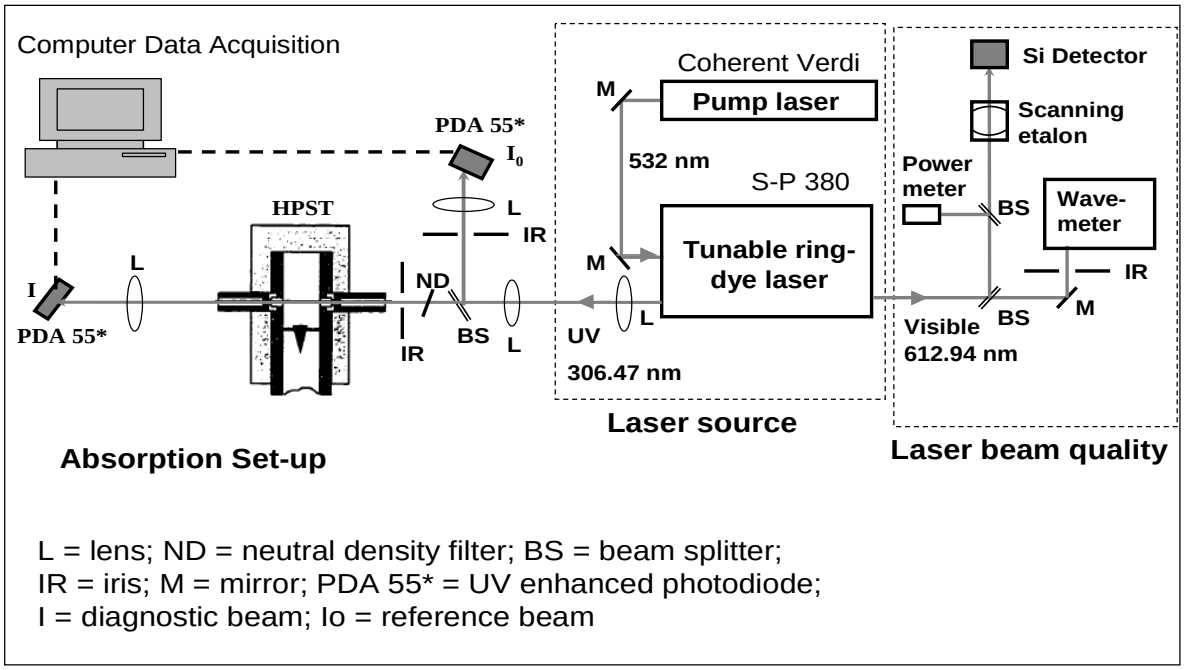

Figure 1. OH laser absorption experimental set-up.

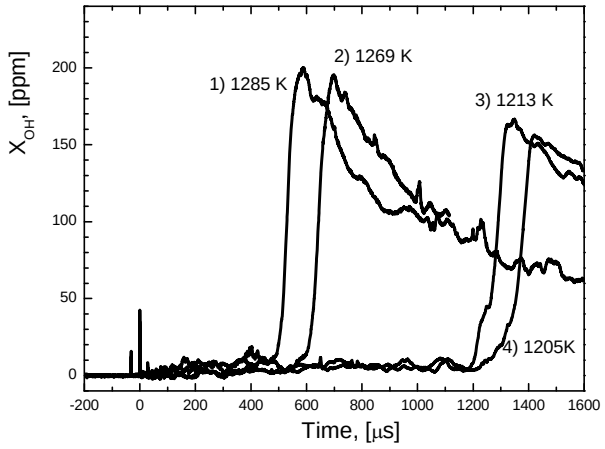

Figure 2. OH absorption data for MCH. Initial mixture: 1000 ppm MCH/O_2/argon, 15 atm, ϕ=0.5. Trace 1: 1285 K; trace 2: 1269 K; trace 3: 1213 K; trace 4: 1205 K.

Development of the CHEMSHOCK Shock Tube Model

A simple gas dynamic model, called CHEMSHOCK, has been developed to predict the temporal evolution of combustion gas temperature and species concentrations behind reflected shock waves with chemical reaction and energy release. CHEMSHOCK provides a convenient simulation method to study various-sized combustion mechanisms over a wide range of conditions. The model consists of two successive sub-operations that are performed on a control mass during each infinitesimal time step: (1) first the gas mixture is allowed to combust at constant internal energy and volume; (2) then the gas is isentropically expanded (or compressed) at frozen composition to the measured pressure. The CHEMSHOCK model was validated against results from a one-dimensional reacting computational fluid dynamics (CFD) code for a representative case of heptane/O_2/Ar mixture using a reduced mechanism. CHEMSHOCK was found to accurately reproduce the results of the CFD calculation with significantly reduced computational time. Further description can be found in Li et al. (2008).

Recent literature has indicated that experimental shock tube ignition delay times for hydrogen combustion at low-temperature conditions may deviate significantly from those predicted by current detailed kinetic models. The source of this difference is uncertain. In the current study, the effects of shock tube facility-dependent gas dynamics and localized pre-ignition energy release were explored by measuring and simulating hydrogen-oxygen ignition delay times. Shock tube hydrogen-oxygen ignition delay time data were taken behind reflected shock waves at temperatures between 908 to 1118 K and pressures between 3.0 to 3.7 atm for two test mixtures: 4% H_2, 2% O_2, balance Ar, and 15% H_2, 18% O_2, balance Ar. See Fig. 3. The

experimental ignition delay times at temperatures below 960 K were found to be shorter than those predicted by current mechanisms when the normal idealized constant volume (V) and internal energy (E) assumptions are employed. However, if non-ideal effects associated with facility performance and energy release are included in the modeling (using CHEMSHOCK, a new model which couples the experimental pressure trace with the constant V,E assumptions), the predicted ignition times more closely follow the experimental data. Applying the new CHEMSHOCK model to current experimental data allowed refinement of the reaction rate for $H+O_2+Ar \leftrightarrow HO_2+Ar$, a key reaction in determining the hydrogen-oxygen ignition delay time in the low-temperature region. Further description can be found in Pang et al. (2008).

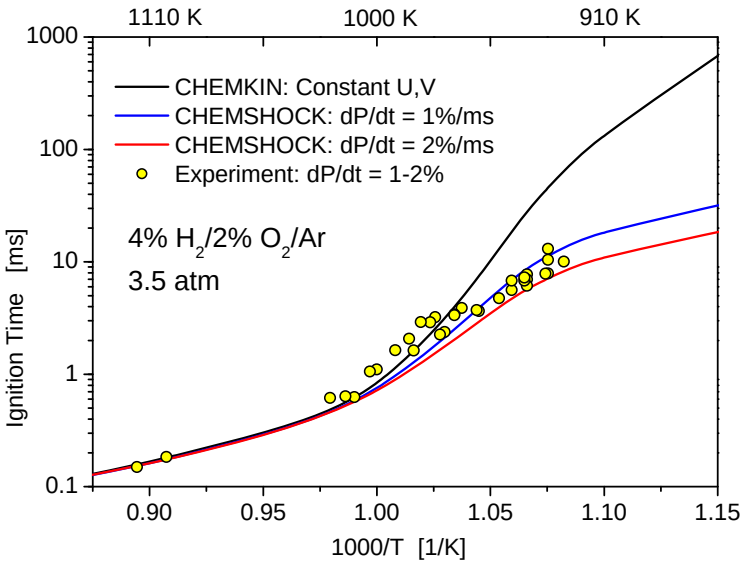

Figure 3. Successful simulation of hydrogen ignition delay time data using CHEMSHOCK. The influence of changing reflected shock pressure, dP/dt, on measured and modeled ignition delay times is shown.

Ignition Delay Time Measurements in Jet Fuel

Ignition delay times were measured for gas-phase jet fuel (Jet-A and JP-8) in air behind reflected shock waves in a heated high-pressure shock tube. Initial reflected shock conditions were as follows: temperatures of 715–1229 K, pressures of 17–51 atm, equivalence ratios of 0.5 and 1, and oxygen concentrations of 10 and 21% in synthetic air. See Fig. 4. Ignition delay times were measured using sidewall pressure and OH* emission at 306 nm. Longer ignition delay times at low temperatures (715–850 K) were accessed by utilizing driver-gas tailoring methods. To our knowledge, for JP-8, these are the first gas-phase shock tube ignition delay time data available, and for Jet-A, these data cover a broader range of conditions than previously available. We found that the ignition delay times for JP-8 and Jet-A, though they have slightly different compositions, have ignition delay times that are very similar. Ignition

delay time variations with pressure, equivalence ratio and oxygen concentration were also investigated. The new experimental results were compared with predictions of several kinetic mechanisms, using different jet fuel surrogate mixtures. Further description can be found in Vasu et al. (2008).

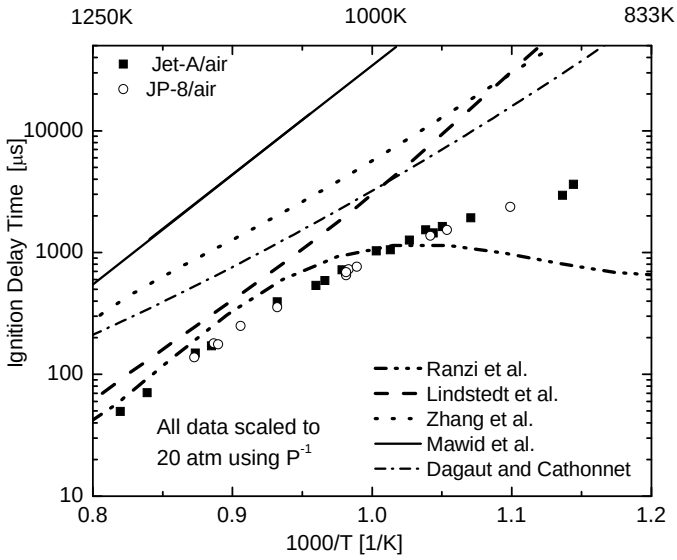

Figure 4. Jet fuel ignition delay times, ϕ = 1 and mechanisms predictions. Violi et al. (2002) #3 surrogate was used with the Ranzi et al. (2006) and the Zhang et al. (2007) mechanisms.

Aerosol Shock Tube Measurements of n-Dodecane and Jet Fuel Ignition Delay Times

A new experimental flow facility, an aerosol shock tube, has been developed to enable studies of shock wave interactions with liquid aerosols, including droplet evaporation kinetics and subsequent chemical reaction of the vapor. This technique provided a uniform spatial distribution of aerosol in the shock tube, which ensured well-behaved shock-induced flows, and a narrow micron-sized aerosol size distribution that rapidly evaporated. These two features enabled quantitative shock tube investigation of the chemistry of high-concentration vapor mixtures of low-vapor-pressure practical fuels and fuel surrogates. In the aerosol shock tube experiments, the incident shock wave was used to vaporize the fuel droplets, and the reflected shock wave was used to induce ignition. See Fig. 5. Using the facility we performed the first aerosol shock tube ignition delay time measurements of n-dodecane/O_2/argon and JP-7/O_2/argon mixtures. See Fig. 6. The measurements were found to be consistent with those made in our heated shock tube facility. Further description can be found in Davidson et al. (2008).

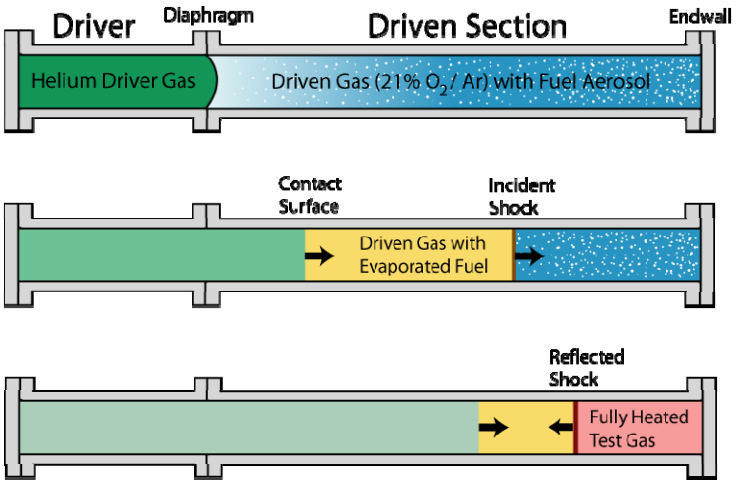

Figure 5. Schematic of operation of aerosol shock tube. The shock tube is filled with aerosol/carrier gas mixture. The incident shock then compresses, heats and evaporates the aerosol, after which the reflected shock raises the fully evaporated test gas mixture to reaction conditions.

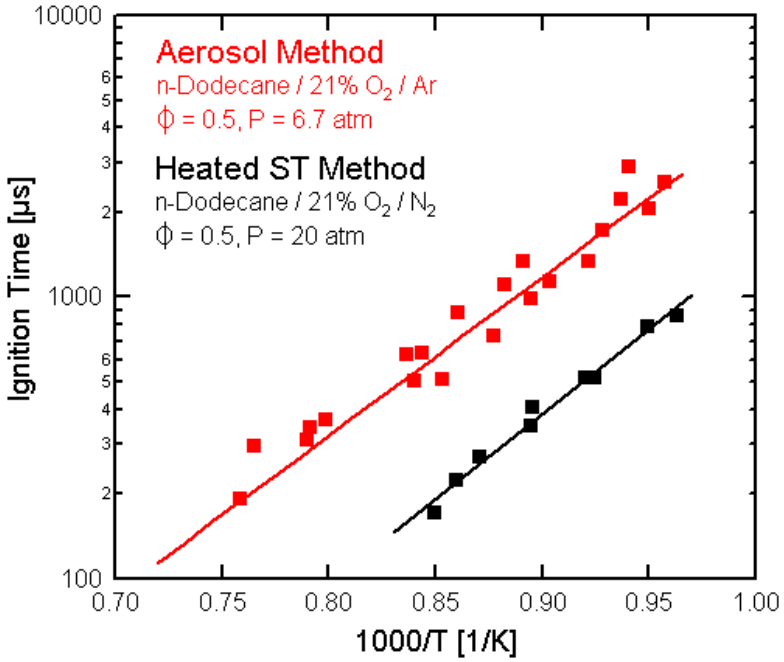

Figure 6. n-Dodecane/21% O_2/argon ignition delay times. Aerosol reflected shock conditions: 6.7 atm, ϕ = 0.5; high-pressure shock tube conditions: 20 atm, ϕ = 0.5, N_2 carrier gas.

High Pressure n-Dodecane Ignition Delay Times and OH Time-Histories Measurements

Ignition delay times and OH concentration time-histories were measured during n-dodecane oxidation behind reflected shocks waves using a heated, high-pressure shock tube. Measurements were made over temperatures of 727 to 1422 K, pressures of 15 to 34 atm, and equivalence ratios of 0.5 and 1.0. See Fig. 7. Ignition delay times were measured using side-wall pressure and OH* emission diagnostics, and OH concentration time-histories were measured using narrow-linewidth ring-dye laser absorption near the R branchhead of the OH A-X (0,0) system at 306.47 nm. Shock tube measurements were compared to model predictions of four current n-dodecane detailed mechanisms for oxidation, and the differences, particularly in the low temperature NTC region where the influence of non-ideal facility effects can be significant, were examined. To our knowledge, these measurements provide the first gas-phase shock tube ignition times and quantitative OH concentration time-histories for n-dodecane oxidation under practical engine conditions, and hence provide benchmark validation targets for refinement of jet fuel detailed kinetic modeling, since n-dodecane is widely used as the principal representative for n-alkanes in jet fuel surrogates. Further description can be found in Vasu et al. (2008).

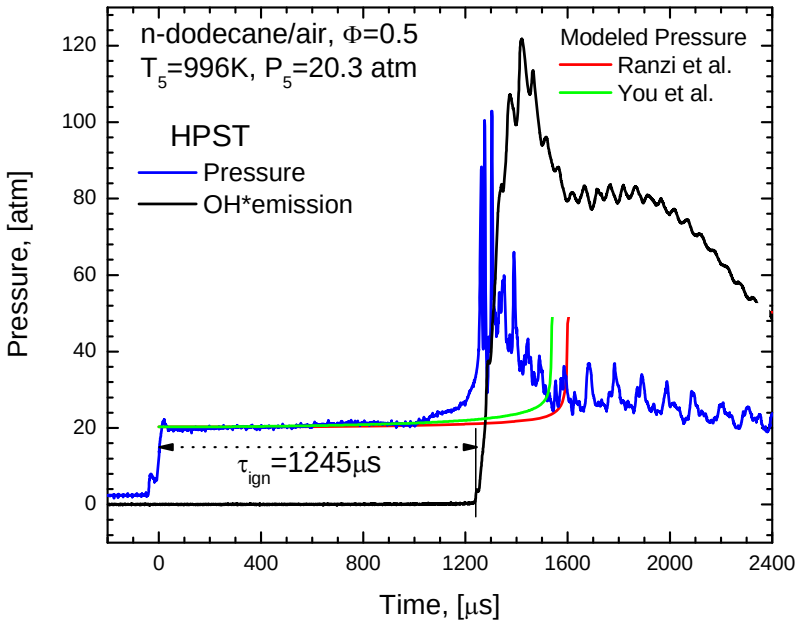

Figure 7. Example n-dodecane/air experimental pressure and OH* emission data. Modeled pressure traces using Ranzi et al. (2006) and You et al. (2008) mechanisms are also shown.

Aerosol Shock Tube Measurements of Diesel Fuel Ignition Delay Times

Shock tube ignition delay times were measured for DF-2 diesel/21% O_2/argon mixtures at pressures from 2.3 to 8.0 atm, equivalence ratios from 0.3 to 1.35, and temperatures from 900 to 1300 K using the aerosol shock tube. This facility combined conventional shock tube methodology with aerosol loading of fuel-oxidizer mixtures. Significant efforts were made to ensure that the aerosol mixtures were spatially-uniform, that the incident shock wave was well-behaved, and that the post-shock conditions and mixture fractions were accurately determined. The nebulizer-generated, narrow, micron-sized aerosol size distribution permitted rapid evaporation of the fuel mixture and enabled experimental separation of the diesel fuel evaporation and diffusion processes that occur behind the incident shock wave, from the chemical ignition processes that occur behind the higher-temperature and -pressure reflected shock wave. This rapid evaporation technique enabled the study of a wide range of low-vapor-pressure practical fuels and fuel surrogates without the complication of fuel cracking that can occur with heated experimental facilities. These diesel ignition delay measurements extended the temperature and pressure range of earlier flow reactor studies, provide evidence for NTC behavior in diesel fuel ignition delay times at lower temperatures, and provide an accurate database for the development and comparison of kinetic mechanisms for diesel fuel and surrogate mixtures. See Fig. 8. Representative comparisons with several single-component diesel surrogate models were also made. Further description can be found in Haylett et al. (2008).

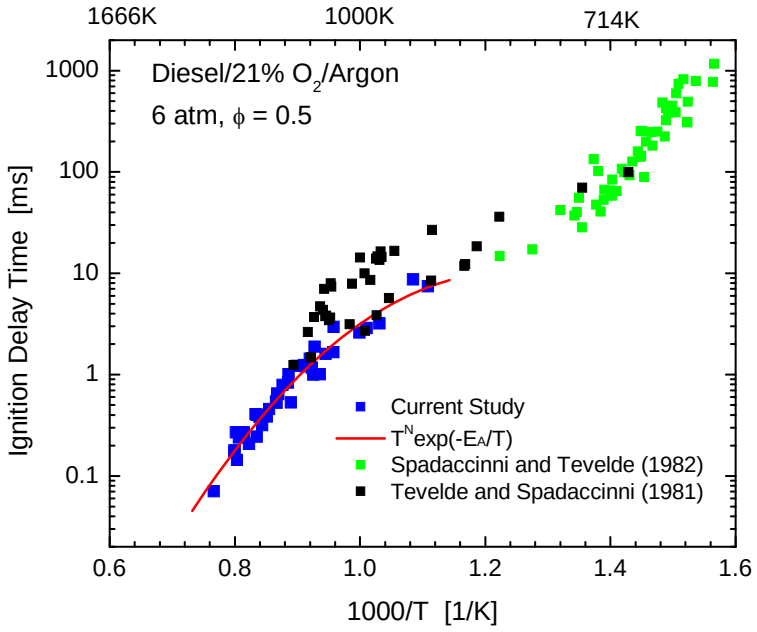

Figure 8. Diesel fuel ignition delay time measurements and comparison with flow tube data of Spadaccini and TeVelde (1982) and TeVelde and Spadaccini (1981).

Mid-IR Laser Absorption Methods for the Detection of Critical Combustion Species

Using a new two-wavelength, mid-IR optical absorption diagnostic that was developed in our laboratory, we simultaneously measured temperature and n-dodecane vapor concentration in an aerosol-laden shock tube. The sensor was used to confirm thermodynamic calculations of post-shock conditions, characterize n-dodecane uniformity, and validate the evaporated-aerosol shock-tube facility as a tool for studying chemistry of low-vapor-pressure fuels. Absorption spectra measured between 323 and 773 K using an FTIR spectrometer were used to select two wavelengths (3409.0 and 3432.4 nm) in the 3400 nm vibrational band for maximum sensitivity to temperature and n-dodecane vapor concentration. Shock-heated mixtures of n-dodecane vapor in argon were used to extend temperature-dependent cross sections at the two selected wavelengths for temperatures ranging from 300 to 1322 K. The two-wavelength sensor is then used to simultaneously measure temperature and concentration after evaporation of a shock-heated n-dodecane aerosol. The signal-to-noise ratio (SNR) of the temperature data was greater than 20 and the SNR of the concentration data was greater than 30. The post-shock temperature and concentration measurements compare favorably with modeled results, providing confidence in the use of this aerosol-shock-tube facility to provide repeatable and well-known thermodynamic conditions. Decomposition rates were extracted from the high-temperature shock data. Good agreement was found between the decomposition rates measured in shock-heated vapor and shock-evaporated aerosol, validating the use of the aerosol shock tube method to examine high-temperature chemistry of low-vapor-pressure species. See Fig. 9. The measured time-resolved n-dodecane concentration data showed a significantly slower decomposition rate than the results of kinetic modeling using two published reaction mechanisms, illustrating the potential for further study of the chemistry of low-vapor-pressure fuels. These results demonstrated the sensitivity and utility of multi-wavelength, tunable mid-IR laser absorption for time-resolved hydrocarbon concentration measurements in environments with time-varying temperature and concentration. Further description can be found in Klingbeil et al. (2007).

We have also measured CO_2 time-histories using 2.7 μm laser absorption during the pyrolysis of three methyl esters: methyl acetate, methyl propionate, and methyl butanoate. These three methyl esters are identical except for their chain length (i.e., have the same degree of saturation.) These measurements were performed at higher concentrations (i.e. 2-3%), where secondary reactions (i.e. H-abstraction reactions) are important. To model these experiments, we have used the improved MB model of Huynh and Violi (2007). Measurements of CO_2 time-histories in methyl esters provide the first necessary kinetics targets for the development of detailed models for bio-fuels and related oxygenated fuel surrogates.

The measurements were carried out behind reflected shock waves using a new class of room-temperature tunable diode lasers near 2.7 μm. The probed transition belongs to the $\nu_1+\nu_3$ combination band of CO_2 that has stronger absorption linestrengths than the bands near 1.5 μm and 2.0 μm used previously to sense CO_2 in combustion gases. Specifically, the band near 2.7 μm is approximately 50 to 1000 times stronger than the bands near 2.0 μm ($\nu_1+2\nu_2+\nu_3$) and 1.55 μm ($2\nu_1+2\nu_2+\nu_3$), respectively. The increased absorption strengths of transitions in this

wavelength region thus offered opportunities for more sensitive and accurate combustion measurements than previous work using the CO_2 bands at shorter wavelength. Representative data are shown in Fig. 10. Further description can be found in Farooq et al. (2008).

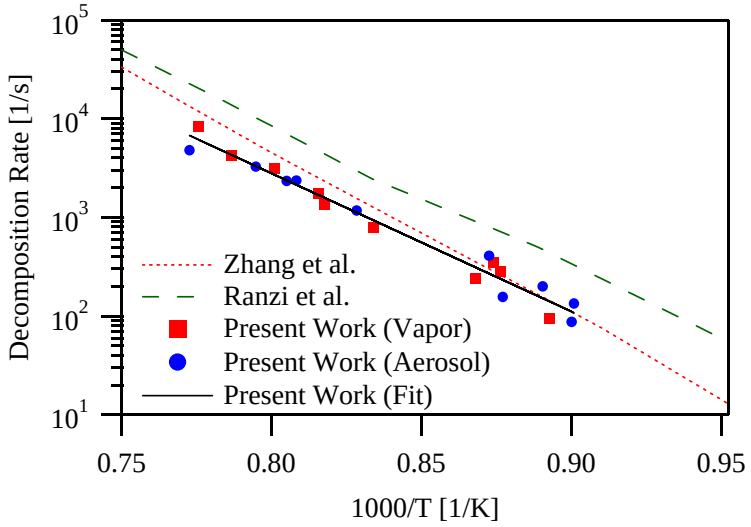

Figure 9. Measured 1/e decomposition rate for shock-heated n-dodecane vapor and aerosol in argon and comparison to two mechanisms.

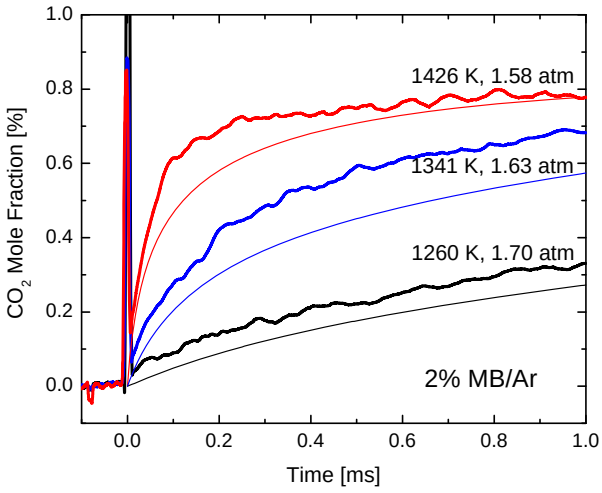

Figure 10. Calculated (light solid) and measured (heavy solid) CO_2 concentration time-histories for methyl butanoate pyrolysis (2% MB in Ar). CO_2 profiles were calculated using an improved MB model of Huynh and Violi (2007).

Deep UV Laser Absorption of Methyl Radicals

Methyl radical concentration time-histories were measured during the oxidation and pyrolysis of iso-octane and n-heptane behind reflected shock waves. Initial reflected shock conditions

covered temperatures of 1100 to 1560 K, pressures of 1.6 to 2.0 atm and initial fuel concentrations of 100 to 500 ppm. Methyl radicals were detected using cw UV laser absorption near 216 nm; three wavelengths were used to compensate for time- and wavelength-dependent interference absorption. Representative data are shown in Fig. 11. Methyl time-histories were compared to the predictions of several current oxidation models. While some agreement was found between modeling and measurement in the early rise, peak and plateau values of methyl, and in the ignition time, none of the current mechanisms accurately recovered all of these features. Sensitivity analysis of the ignition times for both iso-octane and n-heptane showed a strong dependence on the reaction $C_3H_5+H=C_3H_4+H_2$, and a recommended rate was found for this reaction. Sensitivity analysis of the initial rate of CH_3 production during pyrolysis indicated that for both iso-octane and n-heptane, reaction rates for the initial decomposition channels were well isolated, and overall values for these rates were obtained. The present concentration time-history data provide strong constraints on the reaction mechanisms of both iso-octane and n-heptane oxidation, and in conjunction with OH concentration time-histories and ignition delay times, recently measured in our laboratory, should provide a self-consistent set of kinetic targets for the validation and refinement of iso-octane and n-heptane reaction mechanisms. Further description can be found in Davidson et al. (2007).

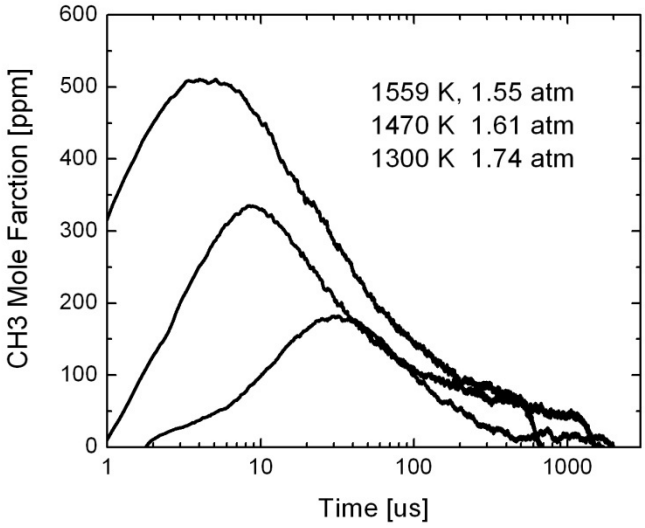

Fig. 11. CH_3 absorption data: iso-octane ignition. Initial conditions: 500 ppm iso-octane, 6250 ppm O_2 in argon. Upper trace, 1559 K; middle trace, 1470 K; lower trace, 1300 K.

Micron-Sized Aerosol Studies

We have developed a suite of tools for studying aerosols behind shock waves. A Mie-extinction particle sizing diagnostic and a computational model, along with a specially designed square-section shock tube were developed to study the time-history of micrometer-sized aerosols

behind shock waves. These tools are critically needed to facilitate the use of shock tubes to study the combustion behavior of low-vapor-pressure fuels. While the facility was designed to study reactive systems, we began by measuring the behavior of water aerosols in the range of 1–10 μm behind shock waves with temperatures between 450 and 600 K and pressures between 0.64 and 1.1 atm. From these data we determined evaporation rates and found a correlation that provides the non-continuum evaporation rate in terms of the d^2 evaporation rate and a correction function. See Fig. 12. Further description can be found in Hanson et al. (2008).

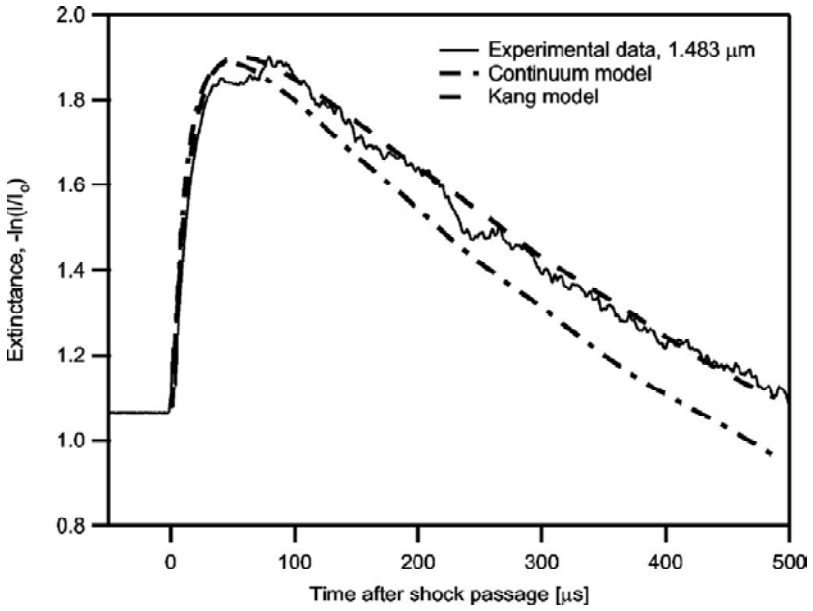

Figure 12. A comparison of experimental extinction data at 1.483 μm with the two runs of the model for a water aerosol in argon. Initial pre-shock conditions were 223 torr, 295 K, mean droplet diameter 2.825 μm, droplet loading 9.9 ppmv, and incident shock speed 513 m/s. Immediately behind the shock, the gas properties are: 0.85 atm and 458 K.

Advances in Shock Tube/Laser Methods for Improved Chemical Kinetics Studies

Shock tubes combined with laser diagnostics provide state-of-the-art capabilities for studying the chemical kinetics of combustion processes. During the past grant period, we have developed several new concepts and methods designed to improve shock tube performance and modeling, extend shock tube operating regimes, provide access to low vapor pressure fuels, and quantitatively measure species time-histories using cw laser absorption. These new methods were developed in the context of studying ignition processes of hydrocarbon fuels at practical engine conditions were used to study the chemical kinetics of real fuels, and to resolve current issues related to shock tube facility effects.

We have improved shock tube performance providing uniform pressure and temperature by reducing (and in some cases effectively eliminating) facility effects by the addition of driver-section inserts and the use of driven section buffer gas volumes. We have extended shock tube test times to greater than 35 ms to access lower temperatures by using driver-section extensions and tailored gas mixtures. See Fig. 13. Further description can be found in Davidson and Hanson (2008).

Fig. 13. 2X extension mounted on kinetics shock tube driver section. The addition of this driver section extension and the use of tailored gas mixtures enabled reflected shock wave experiments with test times of 35 ms.

ARO SUPPORTED PUBLICATIONS: 2004-2007

Peer-Reviewed Archival Publication

H. Li, Z. C. Owens, D. F. Davidson, R. K. Hanson, "A Simple Reactive Gasdynamic Model for the Computation of Gas Temperature and Species Concentration behind Reflected Shock Waves," International Journal of Chemical Kinetics 40 (2008) 189-198.

S. S. Vasu, D. F. Davidson, R. K. Hanson, "Jet Fuel Ignition Delay Times: Shock Tube Experiments over Wide Conditions and Surrogate Model Predictions," Combustion and Flame 152 (2008) 125-143.

D. F. Davidson, D. R. Haylett, R. K. Hanson, "Development of an Aerosol Shock Tube for Kinetic Studies of Low-Vapor-Pressure Fuels", Combustion and Flame, in press.

S. S. Vasu, D. F. Davidson, Z. Hong, V. Vasudevan, R. K. Hanson, "n-Dodecane Oxidation at High Pressures: Measurements of Ignition Delay Times and OH Concentration Time-Histories," accepted for publication, 32nd Combustion Symposium, April 2008.

G. A. Pang, D. F. Davidson, R. K. Hanson, "Experimental Study and Modeling of Shock Tube Ignition Delay Times for Hydrogen-Oxygen-Argon Mixtures at Low Temperatures," accepted for publication, 32nd Combustion Symposium, April 2008.

A. Farooq, D. F. Davidson, R. K. Hanson, L. K. Huynh, A. Violi, "An Experimental and Computational Study of Methyl Ester Decomposition Pathways using Shock Tubes," accepted for publication, 32nd Combustion Symposium, April 2008.

A. E. Klingbeil, J. Porter, J. B. Jeffries, R. K. Hanson "Two-wavelength mid-IR absorption diagnostic for simultaneous measurement of temperature and hydrocarbon fuel concentration," accepted for publication, 32nd Combustion Symposium, April 2008.

D. R. Haylett, D. F. Davidson, R. K. Hanson, "Application of an Aerosol Shock Tube to the Measurement of Diesel Ignition Delay Times," accepted for publication, 32nd Combustion Symposium, April 2008.

A. E. Klingbeil, D. F. Davidson, J. B. Jeffries, R. K. Hanson, "Two-Wavelength Mid-IR Diagnostic for Temperature and n-Dodecane Concentration in an Aerosol Shock Tube," accepted for publication, Applied Physics B.

D. F. Davidson, M. A. Oehlschlaeger, R. K. Hanson, "Methyl Concentration Time Histories during iso-Octane and n-Heptane Oxidation," Proceedings of the Combustion Institute 31 (2007) 321-328.

T. C. Hanson, D. F. Davidson, R. K. Hanson, "Shock Induced Behavior in Micron-Sized Water Aerosols," Physics of Fluids 19 **(**2007) 056104.

H. Li, A. Farooq, J. B. Jeffries, R. K. Hanson, "Near-infrared Diode Laser Absorption Sensor for Rapid Measurements of Temperature and Water Vapor in a Shock Tube," Applied Physics B 89 (2007) 407-416.

A. E. Klingbeil, J. B. Jeffries, R. K. Hanson, "Temperature-Dependent Mid-IR Absorption Spectra of Gaseous Hydrocarbons," J. Quantitative Spectroscopy and Radiative Transfer 107 (2007) 407-420.

E. L. Petersen, R. K. Hanson, "Measurement of Reflected-Shock Bifurcation over a Wide Range of Gas Composition and Pressure," Shock Waves 15 (2006) 333-340.

D. F. Davidson, B. M. Gauthier, R. K. Hanson, "Shock Tube Ignition Measurements of Iso-Octane/Air and Toluene/Air at High pressures," Proceedings of the Combustion Institute 30 (2005) 1175-1182.

V. Vasudevan, D. F. Davidson, R. K. Hanson, "Shock Tube Measurements of Toluene Ignition Times and OH Concentration Time Histories," Proceedings of the Combustion Institute 30 (2005) 1155-1163.

Conference Proceedings

J. B. Jeffries, A. Klingbeil, E. Barbour, A. Farooq, R. K. Hanson, "Mid-Infrared Gas Sensing for Combustion Applications" submitted to Laser Applications to Chemical, Security and Environmental Applications (LACSEA), OSA, St Petersburg FL, March 2008.

G. A. Pang, D. F. Davidson, R. K. Hanson, "Experimental Study and Modeling of Shock Tube Ignition Delay Times for Hydrogen-Oxygen-Argon Mixtures at Low Temperatures," Paper 08S-10, Western States Section/Combustion Institute Spring Meeting, Los Angeles, March 2008.

D. F. Davidson, R. K. Hanson, "Recent Advances in Shock Tube/Laser Diagnostics Methods for Improved Chemical Kinetics Measurements," Paper 08S-01, Western States Section/Combustion Institute Spring Meeting, Los Angeles, March 2008.

S. S. Vasu, D. F. Davidson, R. K. Hanson, "OH Time-History Absorption Measurements at High Pressure and Temperatures Behind Reflected Shocks During Methylcyclohexane Oxidation," Paper 08S-13, Western States Section/Combustion Institute Spring Meeting, Los Angeles, March 2008.

G.A. Pang, D.F. Davidson and R.K. Hanson, "Shock Tube Ignition Delay Times for Hydrogen-Oxygen-Argon Mixtures at Low Temperatures and Elevated Pressures," Paper No. 07F-12, Western States Section/Combustion Institute Fall Meeting, Livermore CA, October 2007.

S. S. Vasu, D. F. Davidson, R. K. Hanson, "Jet Fuel Ignition Delay Times and Modeling: Studies at High Pressures and Low Temperatures in a Shock Tube," Paper No. AIAA-2007-5671, 43rd AIAA Joint Propulsion Conference, July 2007.

S. S. Vasu, D. F. Davidson, R. K. Hanson, "High Pressure Shock Tube Experiments and Modeling of n-Dodecane/Air Ignition," Paper No. P-2730, 26th International Symposium on Shock Waves, July 2007.

A. Farooq, J. Li, J. B. Jeffries, R. K. Hanson, "Measurements of CO2 and H2O near 2.7 microns using Tunable Diode Laser Absorption," AIAA 2007-5015 43rd AIAA Joint Propulsion Conference, Cincinnati, July 2007.

H. Li, A. Farooq, R. D. Cook, D. F. Davidson, J. B. Jeffries, R. K. Hanson, "A Diode Laser Absorption Sensor for Rapid Measurements of Temperature and Water Vapor in a Shock Tube," Paper No. P-2660, 26th International Symposium on Shock Waves, July 2007.

D. R. Haylett, D. F. Davidson, R. K. Hanson, "Development of an Aerosol Shock Tube for Kinetic Studies of Low-Vapor-Pressure Fuels," Paper No. AIAA-2007-5678, 43rd AIAA Joint Propulsion Conference, July 2007.

S. S. Vasu, D. F. Davidson, R. K. Hanson, "Jet Fuel Ignition Delay Times: Shock Tube Investigations at High Pressures," Paper No. 129, 21st ICDERS Meeting, Poitiers France, July 2007.

S. S. Vasu, N. N. Parikh, D. F. Davidson, R. K. Hanson, "Methylcyclohexane Oxidation: Shock Tube Experiments and Modeling over a Wide Range of Pressures and Temperatures," Paper No. D17, 5th U. S. Combustion Meeting, San Diego, March 2007.

A. E. Klingbeil, J. M. Porter, J. B. Jeffries, R. K. Hanson, "Two-Wavelength Mid-IR Absorption Sensor for Simultaneous Temperature and n-Heptane Concentration Experiments" Paper No. GO3 at 5th U. S. Combustion Meeting, San Diego, March 2007.

S. S. Vasu, D. F. Davidson, R. K. Hanson, "Shock Tube Ignition Delay Times and Modeling of Jet Fuel Mixtures," Paper AIAA-2006-4402, 42nd AIAA/ASME/SAE/ASEE Joint Propulsion Conference, Sacramento CA, July 2006.

D. F. Davidson, M. A. Oehlschlaeger, R. K. Hanson, "Methyl Concentration Time Histories during iso-Octane and n-Heptane Oxidation," Paper 05S-61, Western States Section/Combustion Institute Fall Meeting, Stanford CA, October 2005.

S. S. Vasu, D. F. Davidson, R. K. Hanson, "Shock Tube Measurements and Modeling of Ignition Delay Time in Lean Iso-Octane/Air," Int. Symp. Shock Waves 25, June 2005.

T. C. Hanson, D. F. Davidson, R. K. Hanson, "Shock Tube Measurements of Water and n-Dodecane Droplet Evaporation Behind Shock Waves", Paper 2005-0350, 43rd Aerospace Meeting and Exhibit, January 2005, Reno NV.

Reports

D. F. Davidson and R. K. Hanson, "Fundamental Kinetics Database Utilizing Shock Tube Measurements, Vol. 2: Concentration Time-History Measurements" Mech. Eng. Dept. Report, Stanford University, December 2006.

D. F. Davidson and R. K. Hanson, "Fundamental Kinetics Database Utilizing Shock Tube Measurements, Vol. 1: Ignition Delay Time Measurements" Mech. Eng. Dept. Report, Stanford University, November 2005, available at http://hanson.stanford.edu/.

BIBLIOGRAPHY

P. Dagaut, M. Cathonnet, Progress Energy Comb. Sci. 32 (2006) 48-92.

L. K. Huynh, A. Violi, "Thermal decomposition of methyl butanoate: an ab initio study of a biodiesel fuel surrogate," J. Organic Chem. in press.

R.P. Lindstedt, L.Q. Maurice, J. Prop. Power 16 (2) (2000) 187-195.

M.A. Mawid, T.W. Park, B. Sekar, C. Arana, 40th AIAA/ASME/SAE/ASEE Joint Prop. Conf. Exhibit, 2004, Paper No. AIAA 2004-4207.

E. Ranzi, 2006, available at: http://www.chem.polimi.it/CRECKModeling/kinetic.html.

L.J. Spadaccini, J. A. TeVelde, Comb. Flame 46 (1982) 283-300.

J.A. TeVelde, L.J. Spadaccini, Autoignition Characteristics of No. 2 Diesel Fuel, Report No. NASA CR-165315, NASA Lewis Research Center, 1981.

A. Violi, S. Yan, E.G. Eddings, A.F. Sarofim, S. Granata, T. Faravelli, E. Ranzi, Comb. Sci. Tech. 174 (11&12) (2002) 399-417.

X. You, F.N. Egolfopoulos, H. Wang, Proc. Combust. Inst. 32, (2008), Accepted for publication.

R.H. Zhang, E.G. Eddings, A.F. Sarofim, Proc. Combust. Inst. 31 (2007) 401-409; Alias: Utah Surrogate Mechanism: Zhang's MECOFU Version 3 Beta; and R.H. Zhang, Ph.D. dissertation, Department of Chemical Engineering, University of Utah, Salt Lake City, UT, 2005.